Airborne Instruments for the *In Situ* Detection of ClONO$_2$, NO$_2$, ClO, and BrO in the Stratosphere
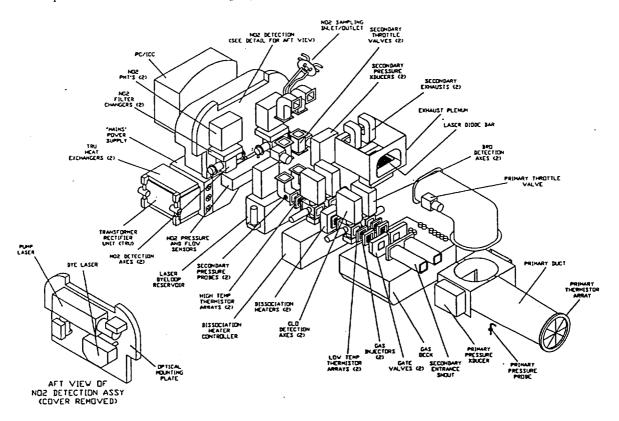
Progress Report
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Scientific Objectives: Development of a new instrument to both further the technology of small, lightweight instruments for robotic aircraft and to achieve the ability to detect $ClONO_2$, NO_2, ClO and BrO from the NASA ER-2 aircraft drove the development of the instrument displayed schematically in Figure 1.

The instrument is tailored for the left superpod of the ER-2.

The addition of this instrument to the current complement of instruments on the ER-2 in conjunction with the deployment of the ER-2 into the high latitude northern hemisphere summer will allow the following objectives to be addressed in the upcoming mission:

- Given the addition of *in situ* observations of $ClONO_2$, does the sum of HCl and chlorine nitrate concentrations equal the inorganic chlorine reservoir inferred from the tracer correlation with organic chlorine? Does the simultaneous observation of $ClONO_2$, NO_2, HCl, OH, HO_2, O_3, CH_4, NO and solar flux yield the same *derivatives* as calculated from the elementary steps in the network of reactions hypothesized to couple those species?

- Given the addition of *in situ* LIF detection of NO_2 (the rate limiting radical in the dominant nitrogen radical catalyzed destruction mechanism of ozone) in combination with HO_2, ClO and BrO that rate limit the hydrogen, chlorine and bromine catalytic cycles respectively, what is the fractional contribution of each of these catalytic cycles to the rate of ozone loss in the high latitude summer? In the mid-latitudes and the tropics?

- Does the loss rate of ozone observed on tracer surfaces match the sum of the rate limiting steps determined directly from observations of HO_2, ClO, BrO and NO_2?

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- Does the free radical catalytic system transition from hydrogen-halogen control to nitrogen radical control in the high latitude summer hemisphere? If the system does transition to nitrogen control, how does that transition take place? Does the transition depend in a critical way on aerosol loading? On temperature? On insolation?
- What is the quantitative impact of the absence of night-time reservoir formation on the inorganic partitioning of species? On the free radical concentrations?
- How is the photochemical structure of the middle-upper troposphere modified in the summer, high latitude period? What are the dominant features of the transition from catalytic destruction of ozone in the lower stratosphere to catalytic production of ozone in the troposphere?
- What are the dominant chemical sources of HO_x in the middle-upper troposphere during high latitude summer? Are proposed sources such as $BrONO_2 + H_2O$ of quantitative importance?
- What is the $[ClO]/[Cl_y]$ ratio and the $[HO_2]/[HO_x]$ ratio as a function of NO_2 concentration? NO_x concentration? NO_y concentration?
- Given the addition of LIF detection of NO_2, does the observed $[NO]/[NO_2]$ ratio match that calculated from the elementary steps? Does the observed [NOx]/[NOy] ratio match that calculated from the elementary steps? Do the derivatives match?
- Penetration into the high-latitudes of the northern hemisphere with multiple flights covering a period of six months provides the opportunity to explore a large dynamic range in species concentrations, temperatures, daylight to darkness ratios, and terminator transit periods. Do the diurnal patterns in species concentrations reveal missing processes?
- By what mechanism and in what pattern is material exchanged between high latitudes and the tropics during NH summer?
- What are the initial conditions of the species concentrations that constitute the arctic vortex for the winter that *follows* the POLARIS campaign?
- What conclusions can be drawn regarding the degree of ozone destruction within the arctic vortex by halogen catalysis during the *previous* winter by investigating the remnants of the vortex in April?

INSTRUMENT PROGRESS REPORT: FIELD TRIALS, CALIBRATION, THERMAL TAILORING.

Section I: Laboratory demonstration of the quantitative conversion of $ClNO_2$ to atomic chlorine by thermal decomposition in the gas phase.

The previous progress report identified a central unresolved problem in the development of the new thermal dissociation technique as the incomplete conversion of chlorine nitrate to atomic chlorine. Absolute calibration data showed that 20–30% of the initial $ClONO_2$ was not appearing as product Cl under a broad range of temperature, pressure and velocity conditions, yet the conversion percentages were consistent and reproducible. Two approaches were taken in the diagnosis of the problem. First, the inclusion of the solid state laser system for the detection of NO_2 was joined to the chlorine nitrate calibration system such that we could simultaneously observe *both* the ClO and NO_2 fragments following thermal dissociation of the parent $ClONO_2$ molecule.

Those experiments showed that 1.0 ± 0.1 NO_2 molecules were produced for each $ClONO_2$ molecule dissociated but that 0.8 ± 0.1 ClO radicals were produced for each $ClONO_2$ molecule dissociated. This both demonstrated the fundamental validity of the thermal dissociation mechanism and placed direct focus on diagnosing the cause of the "missing" atomic chlorine.

The laboratory analysis centered on

* Heterogeneous loss of ClO or Cl
* Thermal gradients in the dissociation region
* Temperature dependence of the Cl absolute calibration
* Gas phase loss of the Cl atom product
* Free radical loss on the silicon strips used to inject the temperature step into the flow.

A series of over one hundred experiments conclusively isolated the cause of the problem to be the increase in optical depth in the O_2 cells at elevated temperature. This increase in optical depth results from the increase in water vapor partial pressure as a function of temperature, releasing water held interstitially in the metal wall of the O_2 cell. This effect begins to be observable at cell temperatures above 40C and becomes increasingly worse with increasing temperature. A decision was made to eliminate the problem categorically by designing an active cooling system using forced cold air extracted from the free stream to cool the O_2 cell directly in combination with the base of the lamp modules and to use the still cool exhaust from the O_2 cell cooling manifold to cool the detector head O_2 cell and the UV monitor. By this technique the operating temperature of the O_2 cells could be kept *below* 0°C during all phases of the flight. That this is so was demonstrated during subsequent flight tests of the ER-2.

Section II: Development of the laser system for the detection of NO_2.

The optical design of the new fiber-optic coupled solid state laser system provides 4 watts of 530 nm light with a pulse rate of 10 kHz and a pulse width of 25 nsec. This translates into an output at the 585 nm transition of NO_2 of 500 mW average power at a rep rate of 10 kHz. In combination with our experience in optical design, this translates into a detection threshold for NO_2 of 10 pptv in an integration time of 60 sec with a signal-to-noise ratio of 5. With planned optical refinements and developments in detector technology, this detection threshold is projected to drop to 1 pptv.

With this laser system as the central optical component, the design of the flight system was finalized and the system was constructed as a subsystem of the instrument shown schematically in Figure 1. The design follows the strategy that the NO_2 laser system and detection system is a completely self-contained optical system with the pump laser, dye laser and laser diagnostic subsystems on one side of a composite bulkhead and the steering optics and detection axes on the other side of the bulkhead. With this arrangement, the laser/detection system in its entirety can be aligned, tested and calibrated while it is external to the flight instrument and then inserted, unaltered, into the flight instrument.

The detection axes consist of two cells, each of which employ a "White cell" for flux amplification, a collection mirror to increase the collection solid angle and a condensing lens in series with interference filters to isolate the spectral region for NO_2 fluorescence in one position and the Raman scattered component in the other position.

The objective of the optical design is to (1) maximize the proportionality factor between the NO_2 concentration and the detector count rate while simultaneously (2) minimizing the scattered light observed by the detector in the absence of NO_2.

The laser is controlled by an on-board computer that turns on the solid state laser, starts the dye pump, checks all interlocks that protect individual subsystems of the laser, monitors the input power to the dye laser and the alignment of the pump laser into the dye laser, tunes the dye laser for maximum output of 585 nm radiation and "chops" the laser line on and off the NO_2 line based on a correlation fit with an on-board NO_2 absorption cell that locks the laser line position to the proper frequency. In addition to laser control, the computer executes predetermined "flight algorithms" that define the experimental configuration throughout the flight, gathers and stores both analog and digital data and executes an ordered shutdown of the system as the aircraft descends.

The flight instrument is tailored to control the running temperatures of each of the subsystems under flight conditions. Flight conditions, in combination with conditions prior to flight that extend from -20°C to +40°C, encompass a very large dynamic range in temperature, pressure and water vapor concentration. Thermal control is achieved by a combination of active heating and cooling using tailored resistive heaters and cold air ram induction methods.

Particular care is given to materials used in (a) the system design that carries the NO_2 sample from the measurement duct within which the $ClONO_2$ is thermally dissociated (a combination of quartz and Teflon) that operates at elevated temperature and delivers the sample to one NO_2 detection axis and (b) the system that extracts a flowing sample of stratospheric air that operates at ambient temperature and delivers a flowing sample to the other NO_2 detection axis.

Section III: Development of the 3 kV Dissociation Heater

A key development in the design of the new instrument centered on the successful development of the dissociation heater that serves to inject heat into the duct such that the temperature can be scanned from ambient to 550°K but such that the radicals formed in the dissociation of $ClONO_2$ are not removed heterogeneously and such that the atomic chlorine formed in the chemical conversion of ClO to Cl is not removed on the heater elements. The assembled array of heating elements must also sustain continued cycling of temperature during laboratory calibration and during extended flights. These objectives have been met by a novel set of silicon strip heaters with imbedded gold contacts. The designed system has passed its chemical, physical, and electronic tests in both laboratory and flight trials, and is now complete.